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(54) **METHOD OF PREVENTING CARBURIZATION OR NITRIDATION, AND PATCH FOR  
PREVENTING CARBURIZATION, NITRIDATION OR OXIDATION**

VERFAHREN ZUR VERHINDERUNG VON AUFKOHLUNG ODER NITRIERUNG, UND FLECKEN  
ZUR VERHINDERUNG VON AUFKOHLUNG, NITRIERUNG ODER OXIDATION

PROCEDE POUR EMPECHER LA CEMENTATION OU LA NITRURATION ET MASQUE POUR  
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no. 164489N, **CEBETEREWICS ANTONI** 'paste  
for protecting steel surfaces during carburizing  
or nitriding'

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## Description

[0001] This invention relates to a patch suitable for preventing carburization, nitriding or oxidation which is used in the case of carburizing or nitriding a portion of a steel or other metallic part to harden the portion while preventing the carburization or nitriding of the other portions to maintain the toughness of the other portions, or used for preventing a metallic part or the like from surface oxidation or carburization due to a heat treatment, and relates also to a method of preventing carburization or nitriding by use of the patch.

[0002] Metallic mechanical parts such as cams, shafts, pistons, pins, etc., used for automobiles, ships and the like are required to be tough, as a whole, and to have a high level of wear resistance at portions thereof subjected to friction. A method of obtaining a mechanical part having both high toughness and wear resistance is known in which a tough steel material is hardened, by carburization or nitriding, only at the portion thereof required to have wear resistance. In this case, masking the other portions of the steel material other than the portion to be hardened is adopted for preventing the other portions from carburization or nitriding, thereby maintaining the toughness of the other portions. On the other hand, in a heat treatment of a metallic part, for instance, there are some cases where oxidation, decarburization or the like of a specified portion of the metallic part must be prevented assuredly. In such a case, the portion to be prevented from oxidation must be masked so as to prevent the contact of the portion with an oxidizing atmospheric gas.

[0003] As a masking material of this type, there have hitherto been used copper plating and tin plating. Because the plating operation for masking is complicated and troublesome, however, a masking material of a coating type for forming a gas barrier film has recently been developed, and has been coming rapidly to wide use. The coating type masking material comprises a powder of a chemical having an anti-carburization, anti-nitriding or anti-oxidation action, such as borax, borosilicic acid, tin powder, etc., blended with small amounts of a resin and a solvent. At the time of a heat treatment such as carburization, nitriding, etc., the coating type masking material is applied to a specified portion of a steel material, and the steel material thus coated is heated to a temperature of from 300 to 1000 °C in a furnace which is charged with a carburizing, nitriding or oxidizing agent or which is filled with a carburizing, nitriding or oxidizing gas atmosphere. Upon the heating, the resin in the coating is lost through thermal decomposition and, simultaneously, the anti-carburizing, anti-nitriding or anti-oxidizing component is fused to the surface of the steel material to form an anti-carburizing, anti-nitriding or anti-oxidizing film. The film thus formed prevents the contact of the coated portion of the steel material with a carburizing, nitriding or oxidizing component, thereby preventing the carburization, nitriding or oxidation of the

coated portion. In this case, if the anti-carburizing, anti-nitriding or anti-oxidizing film is ununiform or has pinhole defects or the like, the intended prevention of carburization, nitriding or oxidation is not achievable. Therefore, it is the most important point here to provide an anti-carburizing, anti-nitriding or anti-oxidizing film which is free of defects and is uniform.

[0004] In the coating material, however, the amount of the resin component serving as a vehicle is small (If the amount is large, decomposed gases will be released in large amounts upon thermal decomposition of the resin component, thereby hindering the fusing of the anti-carburizing, anti-nitriding or anti-oxidizing film to the steel surface portion.), and the coating material is accordingly poor in spreadability. Thus, in order to form a uniform coating, it is necessary for the coating material to be diluted by a solvent and be applied repeatedly. The necessity leads to the need for elaborate work using a brush or the like and for much labor.

[0005] EP-A-0 306 727 relates to a glass powder adhesive sheet comprising a glass powder molding which comprises as main components a glass powder and a resin binder and, if necessary, inorganic powder and/or metal powder, and has provided on the surface thereof an adhesive layer having a thermal decomposition initiation temperature higher than that of the resin binder.

[0006] This invention has been made in consideration of the above-mentioned circumstances.

[0007] It is accordingly an object of this invention to provide a method of preventing carburization or nitriding of an arbitrary portion of a metallic member by use of a material for preventing carburization or nitriding.

[0008] It is another object of this invention to provide the material for preventing carburization, nitriding or oxidation of a patch type which enables formation of a film having an excellent anti-carburization, anti-nitriding or anti-oxidation effect through a simple means.

[0009] The present invention relates to the subject-matter disclosed in the claims.

[0010] The patch suitable for preventing carburization, nitriding or oxidation used in a method according to this invention is a patch-type material comprising a pressure sensitive adhesive layer on one side of a film-shaped material formed from a heat-fusible or heat-meltable particulate material having an anti-carburizing, anti-nitriding or anti-oxidizing action wherein from 20 to 95 parts by weight of said particulate material are blended with from 80 to 5 parts by weight of a heat-decomposable resin as a binder. The patch for preventing carburization, nitriding or oxidation is applied to a portion to be prevented from being carburized, nitrified or oxidized of a metallic member to be subjected to a carburizing, nitriding or oxidizing treatment, and the whole of the metallic member is exposed to carburizing, nitriding or oxidizing conditions, whereby it is possible to carry out carburization, nitriding or oxidation of the non-patched portions of the metallic member while preventing the patched portion from being carburized, nitrified

or oxidized.

[0011] The present inventors have made various studies for developing a new anti-carburizing technique as a substitute for copper plating or anti-carburizing, anti-nitriding or anti-oxidizing coating materials, and, as a result of the studies, have acquired the following idea.

[0012] The present inventors have come to consider that when components for forming a film for preventing carburization, nitriding or oxidation are formed into a film shape and an adhering function, such as the function of a pressure sensitive adhesive tape, is imparted to the film-shaped material, it will be possible to form an anti-carburizing, anti-nitriding or anti-oxidizing film simply by attaching the film-shaped material to a surface of a substrate. As a result of the present inventors' studies for carrying out the idea, it has been confirmed that when a heat-fusible or heat-meltable inorganic powder having an anti-carburization, anti-nitriding or anti-oxidation performance is formed into a film shape by use of a heat-decomposable resin as a binder and the film-shaped material is provided with a pressure sensitive adhesive layer on one side thereof, it is possible to form an anti-carburizing, anti-nitriding or anti-oxidizing film simply by applying the film-shaped material to a portion to be prevented from carburization, nitriding or oxidation. It should be particularly noted in this case that the film comprising the anti-carburizing, anti-nitriding or anti-oxidizing component has such appropriate pliability and strength as to enable application of the film to any portion to be prevented from carburization, nitriding or oxidation and that the resin and the pressure sensitive adhesive are thermally decomposed in a heating step for carburization, nitriding or oxidation, thereby fusing the anti-carburizing, anti-nitriding or anti-oxidizing component securely to the substrate surface in the form of a uniform film free of pinhole defects. In this invention, therefore, a heat-fusible or heat-meltable inorganic material (inclusive of metal) which has an anti-carburizing, anti-nitriding or anti-oxidizing function and which is in a particulate form capable of being kneaded uniformly with the heat-decomposable resin is used as the anti-carburizing, anti-nitriding or anti-oxidizing component. The particles of the particulate material, upon thermal decomposition of the resin, are fused or melted together and fused to the substrate surface to form the anti-carburizing, anti-nitriding or anti-oxidizing film. Materials usable as the particulate material include, for example, borax, boron oxide, borosilicic acid, phenylboric acid, water glass, frit, low melting point glass; powder or crushed foils of metals such as copper, tin, Al, zinc, Ni, etc., and so on. In a preferred embodiment the metal has a melting point of not higher than 900°C. If required, two or more of these materials may be used in combination. The particles of the particulate material may take various shapes on a microscopic basis, such as spheroidal, flaky, pellet-like, short fiber-like, crushed irregular shapes and the like shapes.

[0013] When the particulate material is used together

with an adjuvant, which will be mentioned below, the heat-fusible particulate material is restrained from flowing upon melting under heat, whereby a more uniform gas barrier film is obtainable. In addition, the adjuvant has the function of accelerating the dispersion of the particulate material into the binder, facilitating the formation of the film, or enhancing the surface strength of the film. Materials usable as the adjuvant include, for example, powders of titanium oxide, iron oxide, zinc oxide, talc, calcium carbonate, mica, silica (fumed silica, Aerosil, etc.), alumina, magnesia, silicon carbide, fly-ash, graphite, silicic acid, kaolinite, clay, etc., at least one of which may be used singly or in combination.

[0014] The resin to be used as the binder component for forming the anti-carburizing, anti-nitriding or anti-oxidizing component into a film shape may be any of those resins which have appropriate tensile strength and flexibility and which are lost through thermal decomposition under the carburizing, nitriding or oxidizing conditions. In total consideration of dispersibility of the anti-carburizing, anti-nitriding or anti-oxidizing component, physical properties of the film, cost, etc., the most preferable ones of the usable resins are polyolefin resins such as polyethylene, polypropylene, etc., acrylic resins, polyester resins, polyamide resins, polyurethane resins, natural or synthetic rubbers, and the like, among which especially preferred is polyethylene.

[0015] The mixing ratio of the anti-carburizing, anti-nitriding or anti-oxidizing component and the resin may be determined appropriately, taking into account the physical properties of the composition film obtained, the amount of gases generated upon thermal decomposition, fusibility of the anti-carburizing, anti-nitriding or anti-oxidizing film, the anti-carburization, anti-nitriding or anti-oxidation performance, and so on. If the amount of the resin is too large, however, the amount of the anti-carburizing, anti-nitriding or anti-oxidizing component is reduced relatively, leading to a higher possibility of pinhole defects or the like being generated in the anti-carburizing, anti-nitriding or anti-oxidizing film. Furthermore, the amount of the gases generated upon thermal decomposition of the resin is increased, resulting in poorer fusing of the anti-carburizing, anti-nitriding or anti-oxidizing film to the substrate surface. If the amount of the resin is insufficient, on the other hand, the resultant film becomes fragile with the attendant lowering in pliability, thereby making it difficult to adhere the film securely to the substrate surface by application. Therefore, the anti-carburizing, anti-nitriding or anti-oxidizing component and the binder resin are mixed in a weight ratio (of the component to the resin) of 20-95:80-5, preferably 30-80:70-20, and more preferably 40-70:60-30. The preferable ranges should not be construed as limiting the invention, because the recommendable mixing ratio varies greatly depending on the kinds of the anti-carburizing, anti-nitriding or anti-oxidizing component and the binder resin. The layer constituting the anti-carburizing, anti-nitriding or anti-oxidizing film can be

formed by a method wherein a dope containing the anti-carburizing, anti-nitriding or anti-oxidizing component and the binder resin is cast into a film, a method wherein a molten kneaded mixture of the anti-carburizing, anti-nitriding or anti-oxidizing component and the resin is press molded, or the like methods. Taking into account the workability in molding or forming, etc., the most preferred of these methods is a method in which the anti-carburizing, anti-nitriding or anti-oxidizing component is kneaded into the binder resin (e.g., polyethylene) with heating, and the kneaded mixture is formed into a film by melt extrusion.

**[0016]** The thickness of the film-shaped material comprising the anti-carburizing, anti-nitriding or anti-oxidizing component and the binder resin may be appropriately determined according to the kind of the anti-carburizing, anti-nitriding or anti-oxidizing component, the proportion of the component, or the required degree of prevention of carburization, nitriding or oxidation. The thickness is generally in the range from 100 to 400  $\mu\text{m}$ , preferably from 150 to 300  $\mu\text{m}$ , and more preferably from 180 to 250  $\mu\text{m}$ .

**[0017]** The pressure sensitive adhesive layer provided on one side of the composition film displays the function of adhering the film to a portion to be prevented from being carburized, nitrided or oxidized of a substrate. The pressure sensitive adhesive layer may be any one that shows a pressure sensitive adhesive property at normal temperature, maintains the pressure sensitive adhesiveness sufficient for keeping the film unreleased from the patched portion until the anti-carburizing, anti-nitriding or anti-oxidizing component is melted and fused to the surface of the substrate, and that is capable of thermal decomposition under the carburizing, nitriding or oxidizing conditions. For instance, a pressure sensitive adhesive comprising rosin, a petroleum resin or the like compounded as a pressure sensitive adhesive component in a synthetic or natural rubber, a silicone pressure sensitive adhesive, etc., may be used for forming the pressure sensitive adhesive layer. Where the pressure sensitive adhesive lacks heat resistance, however, the film would be released from the patched portion before the anti-carburizing, anti-nitriding or anti-oxidizing component is melted and fused to the substrate surface. In that case, it is impossible for the film to display the anti-carburizing, anti-nitriding or anti-oxidizing function. It is therefore desirable to use a heat-resistant pressure sensitive adhesive which retains a pressure sensitive adhesive force even at temperatures of not lower than 200°C, preferably not lower than 250°C and, particularly, shows a further increase in the adhesive force when being heated to about 150 °C after applied to a desired portion of the substrate surface. Though a silicone pressure sensitive adhesive may be mentioned as a typical example of the pressure sensitive adhesive having such properties, other pressure sensitive adhesives can also be used, naturally, as the preferable pressure sensitive adhesive.

**[0018]** The pressure sensitive adhesive layer is immediately located between the layer containing the anti-carburizing, anti-nitriding or anti-oxidizing component and the substrate when the film-shaped material is applied to the substrate, and the gases generated upon thermal decomposition of the pressure sensitive adhesive layer are considered to produce a particularly great influence on the fusing of the anti-carburizing, anti-nitriding or anti-oxidizing film to the substrate. Therefore, it is preferable that the pressure sensitive adhesive layer is as thin as possible, in such a range as not to hinder the adhesion upon application to the substrate, and the thickness is desirably controlled to or below about 20  $\mu\text{m}$ . An anti-carburizing, anti-nitriding or anti-oxidizing component may be incorporated in the pressure sensitive adhesive layer in a small amount in such a range as not to hinder the pressure sensitive adhesive property.

**[0019]** The patch according to this invention comprises, fundamentally, the film containing the anti-carburizing, anti-nitriding or anti-oxidizing component and the pressure sensitive adhesive, as mentioned above. In putting the patch into practical use, it is extremely convenient to laminate the film with a release paper on the pressure sensitive adhesive layer side, for enhancing handleability of the patch, and to release the release paper at the time of using the patch. Besides, when the film containing the anti-carburizing, anti-nitriding or anti-oxidizing component is laminated on the upper side thereof with a resin film, a paper, a synthetic paper or the like as a support layer, the film containing the anti-carburizing, anti-nitriding or anti-oxidizing component, even if somewhat brittle, is advantageously reinforced by the support layer. Furthermore, a trade name, directions for use or the like may be printed on the support layer.

**[0020]** Where the patch according to this invention is commercialized in the form of a roll of an elongate patch material, a release agent may be applied to the surface of the support layer and the patch material be rolled with the pressure sensitive adhesive layer in contact with the release agent.

**[0021]** The constituents, operation and effect of this invention will now be described in detail while referring to the following examples and comparative examples, it being to be understood that the examples are not to be construed as limiting the invention.

#### Example 1

**[0022]** A silicone pressure sensitive adhesive (trade name "KR-120", a product by The Shin-Etsu Chemical Co., Ltd.) was applied to a release paper, and dried to form a pressure sensitive adhesive layer 10  $\mu\text{m}$  thick. Separately, a  $\text{B}_2\text{O}_3$  powder as an anti-carburizing component was mixed with an acrylic resin (trade name "Acrylic A-126-50", a product by Dainippon Ink & Chemicals, Inc.) in solid matter weight ratios of 8/2 and

9/1, and each of the resultant mixtures was kneaded uniformly. Each of the kneaded mixtures was applied to the pressure sensitive adhesive layer in such an amount as to obtain a dry film thickness of 200  $\mu\text{m}$ , and dried to form a film. The release paper was released from each of the thus obtained films, and the film was applied to a round bar of SCM 415 steel along the circumference of the bar. The round bars with the film applied thereto were placed in a vacuum carburizing furnace, and preheated at 700 °C for 30 minutes. Then, the bars were carburized for 1 hour under the conditions of 1040°C and 40 kPa (300 Torr) by blowing a methane gas into the furnace, then maintained at 800°C for 1 hour, and quenched in oil. After the carburization was over, it was confirmed that a uniform anti-carburizing film was still remaining at the patched portions of the round bars. Upon oil quenching, the film was released completely, leaving little stain. The test pieces were split along the lengthwise direction thereof, and subjected to observation of the carburized condition. It was found that the patched portions had not been carburized at all, which indicates the excellent anti-carburizing effect of the patches.

#### Example 2

[0023] A  $\text{B}_2\text{O}_3$  powder as an anti-carburizing component was admixed with 10% by weight of titanium oxide as a coloring agent to prepare a powdery filler. The filler was mixed with a polyester resin (trade name "Polyester LP-035", a product by The Nippon Synthetic Chemical Industry Co., Ltd.) in a solid matter weight ratio of 7/3, followed by kneading and dispersing. The resultant mixture was applied to a 20- $\mu\text{m}$  thick aluminum foil in a dry film thickness of 200  $\mu\text{m}$ . The film thus obtained was coated with a silicone pressure sensitive adhesive (trade name "YR-3286", a product by Toshiba Silicone Co., Ltd.) in a thickness of 15  $\mu\text{m}$  to form a pressure sensitive adhesive layer. A release paper was placed on the pressure sensitive adhesive layer to obtain a specimen.

[0024] The release paper was released from the film obtained as above, and the film was subjected to an anti-carburization test under the same conditions as in Example 1, upon which a good anti-carburizing effect was observed. The aluminum foil layer, exposed to the surface, did not show any hindrance to the anti-carburizing effect. Instead, the aluminum foil layer was found to make it easier for the film to conform to bending at the time of application to the steel under test, and was found to serve to reinforce the film.

#### Example 3

[0025] An anti-carburizing component consisting of borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) and phenylboric acid ( $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$ ) in a weight ratio of 95/5 was kneaded with molding polyethylene pellets (trade name "D-1021", a product by

Sumitomo Chemical Co., Ltd.) in a weight ratio of the anti-carburizing component to polyethylene of 30/70 in a heating-type kneader to prepare a compound, which was then press molded to be a 300  $\mu\text{m}$  thick film. The same pressure sensitive adhesive as used in Example 2 was applied to one side of the thus obtained film in a thickness of 10  $\mu\text{m}$ , thereby forming a pressure sensitive adhesive layer, and a release paper was attached to the layer to obtain an anti-carburizing film.

[0026] The release paper was removed from the anti-carburizing film obtained as above, then the film was applied to a steel material (S15CK), and the steel material with the film thereon was subjected to a 950 °C  $\times$  5 hr carburization test by a solid carburization method.

[0027] Upon the carburization test, the patched portion was found to have not been carburized, indicating a good anti-carburizing effect of the anti-carburizing film. The portion at which the anti-carburizing effect was confirmed was subjected to X-ray analysis, which revealed no presence of boron or silicon used as the anti-carburizing material, and revealed the absence of any foreign matter mixed into the steel. Besides, polyethylene is pliable and has sufficient film strength for handling.

#### Example 4

[0028] By using boron oxide as an anti-carburizing component and polyethylene in a weight ratio of 50/50, a compound was prepared in the same manner as in Example 3. The compound was extruded at 160°C to form a film 40 cm wide and 200  $\mu\text{m}$  thick.

[0029] The same pressure sensitive adhesive as used in Example 2 was applied to one side of the thus obtained film to form a 15  $\mu\text{m}$  thick pressure sensitive adhesive layer, whereas a silicone release agent (trade name "KS-716", a product by The Shin-Etsu Chemical Co., Ltd.) was applied to the other side of the film to form a release layer. The film was made to be a rolled type test film.

[0030] A sample cut from the rolled film was applied to a steel material (SAE 5120), and subjected to a carburization test by a gas carburization method. The carburization was carried out at 930°C for 5 hours, followed by homogenizing at 930°C for 30 minutes, and by primary quenching in oil after 880 °C  $\times$  30 min heating. As a result, the portion to which the film had been applied showed no carburization. The surface hardness of the quenched steel material was measured by a Vickers hardness test, which gave a hardness value of 880 for the carburized portion and a hardness value of 285 for the portion prevented from carburization. Thus, a good anti-carburizing effect was confirmed. Besides, the film was easy to remove after the test.

#### Example 5

[0031] A mixture of 50 parts by weight of low density polyethylene, 45 parts by weight of boron oxide, 3.5

parts by weight of titanium oxide and 1.5 parts by weight of Aerosil was kneaded with heating in a kneader, and the kneaded mixture was melt extruded at 259°C to prepare a film 300 µm thick. An acrylic pressure sensitive adhesive (trade name "AS-6000", a product by Ipposha Oil Industries Co., Ltd.) was applied to one side of the film in a coating weight of 30 g/m<sup>2</sup> as solids, to obtain an anti-carburizing patch.

[0032] The patch was applied to a round steel bar (S55CK), and a 900 °C × 5 hr carburization test was carried out by a solid carburization method.

[0033] After the carburization test, the patch was removed to examine the carburized condition of the steel bar. The patched portion was found to be little carburized, and the good anti-carburizing effect of the patch was thus confirmed. Upon an X-ray analysis of the portion prevented from carburization, boron oxide used as the anti-carburizing material was not recognized to be mixed in the portion.

#### Example 6

[0034] A mixture of 50 parts by weight of low density polyethylene with 50 parts by weight of 350-mesh crushed tin powder (a product by Fukuda Metal Foil & Powder Co., Ltd.) was kneaded with heating in a kneader, and the kneaded mixture was melt extruded at 250°C to be a film 250 µm thick. A silicone pressure sensitive adhesive (trade name "K-120", a product by The Shin-Etsu Chemical Co., Ltd.) was applied to the back side of the film in a thickness upon drying of 10 µm, to obtain an anti-nitriding patch.

[0035] The anti-nitriding patch was applied to an Al-Cr-Mo steel bar having a carbon content of from 0.35 to 0.5%. After the steel bar with the patch thereon was subjected to a 500°C × 25 hr nitriding treatment, the patch was removed to observe the structure of the surface of the steel. It was confirmed upon the observation that the patched portion had been prevented substantially perfectly from being nitrided.

#### Example 7

[0036] A mixture of 50 parts by weight of low density polyethylene, 20 parts by weight of boron oxide, 4 parts by weight of titanium oxide, 24.9 parts by weight of borosilicic acid frit and 1.5 parts by weight of Aerosil was kneaded with heating in a kneader, and the kneaded mixture was melt extruded at 250°C to be a film 250 µm thick.

[0037] An acrylic pressure sensitive adhesive (trade name "AS-6000", a product by Ipposha Oil Industries Co., Ltd.) was applied to one side of the film in a coating weight of 30 g/m<sup>2</sup> as solids, to obtain an anti-oxidizing patch. The patch was applied to a stainless steel bar (SUS 304), and the steel bar with the patch thereon was subjected to an oxidizing treatment at 1000 °C for 1 hour. After the oxidizing treatment, the patch was re-

moved to examine the oxidized condition of the steel. The examination confirmed that the patched portion had not been oxidized at all.

#### 5 Example 8

[0038] A mixture of 30 parts by weight of an ethylene-vinyl acetate copolymer (trade name "E-2031", a product by Sumitomo Chemical Co., Ltd.), 65 parts by weight of boron oxide and 5 parts by weight of iron oxide (red oxide) was kneaded with heating in a kneader, and the kneaded mixture was melt extruded at 230°C to form a film 120 µm thick. A silicone pressure sensitive adhesive (trade name "YR-3340", a product by Toshiba Silicone Co., Ltd.) was applied to one side of the film in a thickness upon drying of 10 µm, to obtain an anti-carburizing patch.

[0039] The patch was applied to a Cr-Mo steel bar, and the steel bar with the patch thereon was subjected to a gas carburization treatment at 940°C for 13 hours. After the treatment, the patch was removed, and measurement of Rockwell hardness was carried out to examine the anti-carburizing effect of the patch. The hardness of the patched portion was much lower than the hardness of the non-patched portions, which confirms that carburization of the patched portion had been prevented substantially perfectly.

#### Comparative Example 1

[0040] An anti-carburizing paint "Ceramic Paint No. 2", a product by Nippon Kagaku Engineering Co., Ltd., was applied once, twice or thrice to the same SCM 415 steel bar as used in the Examples, along the circumference of the bar. The dry film thickness of the coating was about 100 µm per application. The bar with the coatings thereon was subjected to the same carburization test as in Example 1. It was confirmed upon the test that the portion coated thrice with the anti-carburizing paint had been prevented substantially perfectly from carburization, but the portion coated once and the portion coated twice showed, in part, unsatisfactory prevention of carburization and were unsatisfactory in reliability of toughness.

[0041] This invention, constituted as described above, provides a patch-type material for preventing carburization, nitriding or oxidation which makes it possible to simplify remarkably the masking operation for prevention of carburization, nitriding or oxidation and to obtain a highly reliable preventive effect on carburization, nitriding or oxidation. In addition, the patch according to the invention is capable of being commercialized in the form of labels or a roll of elongate material, and is therefore convenient for handling, transportation, storage, etc., and extremely high in practicability.

**Claims**

1. A method of preventing carburization or nitriding of a portion of a metallic member to be heat-treated which comprises applying a patch suitable for preventing carburization or nitriding which comprises a film-shaped material formed from a heat-fusible or heat-meltable particulate material having an anti-carburizing or anti-nitriding effect, wherein from 20 to 95 parts by weight of said particulate material are blended with from 80 to 5 parts by weight of a heat-decomposable resin as a binder, and a pressure sensitive adhesive material provided on one side of the film-shaped material, through pressure sensitive adhesion to said portion of the metallic member.
2. The method according to claim 1, wherein the particulate material is at least one member selected from borax, boron oxide, borosilicic acid, phenylboric acid, water glass, frit, low melting point glass, or a powder or crushed foil of a metal having a melting point of not higher than 900°C.
3. The method according to claim 1, wherein the particulate material is a powder or crushed foil of at least one metal selected from copper, tin, aluminum, zinc or nickel.
4. The method according to any one of claims 1 to 3, wherein the heat-decomposable resin is at least one member selected from a polyolefin resin, an acrylic resin, a polyester resin, a polyamide resin, a polyurethane resin, a natural rubber or a synthetic rubber.
5. The method according to claim 4, wherein the heat-decomposable resin is a homopolymer or copolymer of ethylene.
6. The method according to claim 1, wherein from 80 to 30 parts by weight of the particulate material are blended with from 20 to 70 parts by weight of the heat-decomposable resin.
7. The method according to claim 6, wherein from 70 to 40 parts by weight of the particulate material are blended with from 30 to 60 parts by weight of the heat-decomposable resin.
8. The method according to any one of claims 1 to 7, wherein the film thickness of a layer constituting the film-shaped material for preventing carburization or nitriding is from 100 to 400 µm.
9. The method according to any one of claims 1 to 8, wherein the layer constituting the film-shaped material for preventing carburization or nitriding is formed in a film shape by a melt extrusion method

from a heated and kneaded mixture of the heat-decomposable resin and the heat-fusible or heat-meltable particulate material having the anti-carburizing or anti-nitriding effect.

10. The method according to any one of claims 1 to 9, wherein an inhibitor of flow of the heat-meltable particulate material at the time of heating is incorporated as an adjuvant in the layer constituting the film-shaped material for preventing carburization or nitriding.
11. The method according to claim 10, wherein the adjuvant is at least one member selected from titanium oxide, iron oxide, zinc oxide, talc, calcium carbonate, silica, aluminum silicate, alumina, zircon, zirconia, magnesia, silicon carbide, fly-ash, graphite or kaolinite.
12. The method according to any one of claims 1 to 11, wherein the pressure sensitive adhesive is a heat-decomposable pressure sensitive adhesive which is decomposed at a carburizing or nitriding temperature.
13. The method according to claim 12, wherein the pressure sensitive adhesive is a silicone pressure sensitive adhesive.
14. The method according to any one of claims 1 to 13, wherein a support layer is provided on the layer constituting the film-shaped material suitable for preventing carburization or nitriding on the side opposite to the pressure sensitive adhesive layer.
15. The method according to any one of claims 1 to 14, wherein a release paper is attached to the lower side of the pressure sensitive adhesive layer.
16. A patch suitable for preventing carburization, nitriding or oxidation which comprises a film-shaped material formed from a heat-fusible or heat-meltable particulate material having an anti-carburizing, anti-nitriding or anti-oxidizing effect, wherein from 20 to 95 parts by weight of said particulate material are blended with from 80 to 5 parts by weight of a heat-decomposable resin as a binder, and a pressure sensitive adhesive material provided on one side of the film-shaped material, with the proviso that the heat-fusible or heat-meltable particulate material is not glass powder.

**Patentansprüche**

1. Verfahren zur Verhinderung der Aufkohlung oder Nitrierung eines Teils eines wärmebehandelnden Metallteils, umfassend das Aufbringen eines zur

- Verhinderung der Aufkohlung oder Nitrierung geeigneten Fleckens, welcher ein filmartiges Material, das aus einem durch Wärme verschmelzbaren oder wärmeschmelzbaren, aus Teilchen bestehendem Material mit Antiaufkohlungs- oder Antinitrierungswirkung hergestellt ist, wobei 20 bis 95 Gew.-Teile des aus Teilchen bestehenden Materials mit 80 bis 5 Gew.-Teilen eines durch Wärme zersetzbaren Harzes als Bindemittel vermischt sind, und ein Haftklebematerial, das auf eine Seite des filmartigen Materials aufgebracht ist, umfaßt, durch Haftklebeadhäsion auf dem Teil des Metallteils.
2. Verfahren nach Anspruch 1, wobei das aus Teilchen bestehende Material mindestens eines ist, das aus Borax, Boroxid, Borkieselsäure, Phenylborsäure, Wasserglas, Glasmasse, Glas mit niedrigem Schmelzpunkt, oder einem Pulver oder zerkleinerten Folie eines Metalls mit einem Schmelzpunkt von nicht größer als 900°C, ausgewählt ist.
  3. Verfahren nach Anspruch 1, wobei das aus Teilchen bestehende Material ein Pulver oder eine zerkleinerte Folie aus mindestens einem Metall, ausgewählt aus Kupfer, Zinn, Aluminium, Zink oder Nickel, ist.
  4. Verfahren nach einem der Ansprüche 1 bis 3, wobei das durch Wärme zersetzbare Harz mindestens eines ist, das aus einem Polyolefinharz, einem Acrylharz, einem Polyesterharz, einem Polyamidharz, einem Polyurethanharz, natürlichem Kautschuk oder synthetischem Kautschuk ausgewählt ist.
  5. Verfahren nach Anspruch 4, wobei das durch Wärme zersetzbare Harz ein Homopolymer oder Copolymer von Ethylen ist.
  6. Verfahren nach Anspruch 1, wobei 80 bis 30 Gew.-Teile des aus Teilchen bestehenden Materials mit 20 bis 70 Gew.-Teilen des durch Wärme zersetzbaren Harzes vermischt sind.
  7. Verfahren nach Anspruch 6, wobei 70 bis 40 Gew.-Teile des aus Teilchen bestehenden Materials mit 30 bis 60 Gew.-Teilen des durch Wärme zersetzbaren Harzes vermischt sind.
  8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Filmdicke der Schicht, die das filmartige Material zur Verhinderung der Aufkohlung oder Nitrierung bildet, 100 bis 400 µm beträgt.
  9. Verfahren nach einem der Ansprüche 1 bis 8, wobei die Schicht, die das filmartige Material zur Verhinderung der Aufkohlung oder Nitrierung bildet, durch ein Schmelzextrusionsverfahren aus einem erwärmten und gekneteten Gemisch aus einem durch Wärme zersetzbaren Harz und einem durch Wärme verschmelzbaren oder wärmeschmelzbaren, aus Teilchen bestehenden Material mit Antiaufkohlungs- oder Antinitrierungswirkung in Form eines Films hergestellt ist.
  10. Verfahren nach einem der Ansprüche 1 bis 9, wobei in die schicht, die das filmartige Material zur Verhinderung der Aufkohlung oder Nitrierung bildet, ein Fließinhibierungsmittel für das wärmeschmelzbare, aus Teilchen bestehende Material für die Zeitdauer des Erhitzens als Hilfsmittel eingebracht ist.
  11. Verfahren nach Anspruch 10, wobei das Hilfsmittel mindestens eines ist, das aus Titanoxid, Eisenoxid, Zinkoxid, Talk, Calciumcarbonat, Siliciumoxid, Aluminiumsilikat, Aluminiumoxid, Zirkon, Zirkoniumoxid, Magnesiumoxid, Siliciumcarbid, Flugasche, Graphit oder Kaolinit ausgewählt ist.
  12. Verfahren nach einem der Ansprüche 1 bis 11, wobei der Haftkleber ein durch Wärme zersetzbarer Haftkleber ist, der bei der Aufkohlungs- oder Nitrierungstemperatur zersetzt wird.
  13. Verfahren nach Anspruch 12, wobei der Haftkleber ein Silikonhaftkleber ist.
  14. Verfahren nach einem der Ansprüche 1 bis 13, wobei eine Trägerschicht auf der Schicht, die das zur Verhinderung der Aufkohlung oder Nitrierung geeignete, filmartige Material bildet, auf der der Haftkleberschicht gegenüberliegenden Seite aufgebracht ist.
  15. Verfahren nach einem der Ansprüche 1 bis 14, wobei ein Trennpapier auf der Unterseite der Haftkleberschicht angebracht ist.
  16. Zur Verhinderung der Aufkohlung, Nitrierung oder Oxidation geeigneter Flecken, umfassend ein filmartiges Material, das aus einem durch Wärme verschmelzbaren oder wärmeschmelzbaren, aus Teilchen bestehenden Material mit Antiaufkohlungs-, Antinitrierungs- oder Antioxidationswirkung hergestellt ist, wobei 20 bis 9 Gew.-Teile des aus Teilchen bestehenden Materials mit 80 bis 5 Gew.-Teilen eines durch Wärme zersetzbaren Harzes als Bindemittel vermischt sind, und ein Haftklebematerial, das auf einer Seite des filmartigen Materials aufgebracht ist, mit der Maßgabe, daß das durch Wärme verschmelzbare oder wärmeschmelzbare, aus Teilchen bestehende Material nicht Glaspulver ist.



## Revendications

1. Procédé pour empêcher la cémentation au carbone ou la nitruration d'une partie d'un élément métallique devant subir un traitement thermique qui comprend l'application d'une pièce ("patch") adaptée pour empêcher la cémentation au carbone ou la nitruration, qui comprend un matériau sous forme de pellicule formé à partir d'une matière particulaire thermofusible ou thermofondante ("heat-meltable") ayant un effet anti-cémentation au carbone ou anti-nitruration, dans lequel de 20 à 95 parties en poids de ladite matière particulaire sont mélangées avec de 80 à 5 parties en poids d'une résine thermodécomposable en tant que liant, et une matière adhésive autocollante prévue sur une face du matériau sous forme de pellicule, par auto-adhérence à ladite partie de l'élément métallique. 5 10
2. Procédé selon la revendication 1, dans lequel la matière particulaire est au moins un élément choisi parmi le borax, l'oxyde de bore, l'acide borosilicique, l'acide phénylborique, le verre soluble, la fritte, le verre à bas point de fusion ou une poudre ou feuille broyée d'un métal ayant un point de fusion ne dépassant pas 900°C. 20 25
3. Procédé selon la revendication 1, dans lequel la matière particulaire est une poudre ou feuille broyée d'au moins un métal choisi parmi le cuivre, l'étain, l'aluminium ou le nickel. 30
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la résine thermodécomposable est au moins un élément choisi parmi une résine de polyoléfine, une résine acrylique, une résine polyester, une résine polyamide, une résine polyuréthane, un caoutchouc naturel ou un caoutchouc synthétique. 35
5. Procédé selon la revendication 4, dans lequel la résine thermodécomposable est un homopolymère ou un copolymère de l'éthylène. 40
6. Procédé selon la revendication 1, dans lequel de 80 à 30 parties en poids de la matière particulaire sont mélangées avec de 20 à 70 parties en poids de la résine thermodécomposable. 45
7. Procédé selon la revendication 6, dans lequel de 70 à 40 parties en poids de la matière particulaire sont mélangées avec de 30 à 60 parties en poids de la résine thermodécomposable. 50
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel l'épaisseur de film d'une couche constituant le matériau sous forme de pellicule pour empêcher la cémentation au carbone ou la nitruration est de 100 à 400 µm. 55
9. Procédé selon l'une quelconque des revendications 1 à 8, dans lequel la couche constituant le matériau sous forme de pellicule pour empêcher la cémentation au carbone ou la nitruration est formée sous forme de pellicule par un procédé d'extrusion à l'état fondu à partir d'un mélange chauffé et malaxé de la résine thermodécomposable et de la matière particulaire thermofusible ou thermofondante ayant un effet anti-cémentation au carbone ou anti-nitruration.
10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel un inhibiteur d'écoulement de la matière particulaire thermofondante est incorporé comme adjuvant au moment du chauffage dans la couche constituant le matériau sous forme de pellicule afin d'empêcher la cémentation au carbone ou la nitruration.
11. Procédé selon la revendication 10, dans lequel l'adjuvant est au moins un élément choisi parmi l'oxyde de titane, l'oxyde de fer, l'oxyde de zinc, le talc, le carbonate de calcium, la silice, le silicate d'aluminium, l'alumine, la zircone, le zirconium, la magnésie, le carbure de silicium, la cendre volante, le graphite ou la kaolinite.
12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel l'adhésif autocollant est un adhésif autocollant thermodécomposable qui est décomposé à une température de cémentation au carbone ou de nitruration.
13. Procédé selon la revendication 12, dans lequel l'adhésif autocollant est un adhésif autocollant à la silicone.
14. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel une couche support est prévue sur la couche constituant le matériau sous forme de pellicule adapté pour empêcher la cémentation au carbone ou la nitruration sur la face opposée à la couche adhésive autocollante.
15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel un papier anti-adhérent est fixé sur la face inférieure de la couche adhésive autocollante.
16. Pièce adaptée pour empêcher la cémentation au carbone, la nitruration ou l'oxydation qui comprend un matériau sous forme de pellicule formé à partir d'une matière particulaire thermofusible ou thermofondante ayant un effet anti-cémentation au carbone, anti-nitruration ou anti-oxydation, dans laquelle de 20 à 95 parties en poids de

ladite matière particulaire sont mélangées à de 80 à 5 parties en poids d'une résine thermodécomposable comme liant, et un matériau adhésif autocollant prévu sur une face du matériau sous forme de pellicule, à condition que la matière particulaire 5 thermofusible ou thermofondante ne soit pas de la poudre de verre.

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